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SHOCK INITIATION OF LOW-DENSITY PRESSINGS
OF AMMONIUM PERCHLORATE

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ABSTRACT

Initiation and detonation behavior of 13-micron ammonium per-
chlorate was studied at loading density 1.00 g/cm^3. Steady detonation
velocities were determined experimentally at three diameters and ex-
trapolated to 3.75 ± 0.15 mm/μsec at infinite diameter. Calculations
with the BKW equation of state gave 4.25 mm/μsec--as good agree-
ment as could be expected for a low-energy chlorine-containing explo-
sive. By introducing 24-kbar flat-topped plane shocks into pellets of
various lengths, it was determined that steady full-strength detonation
was reached after about 15 mm travel. The growth of pressure in the
accelerating wave was followed approximately by means of free-surface
measurements on thin Plexiglas at the top surfaces of the pellets, and
these measurements indicated the pressure to be 55 ± 10 kbar in the
full-strength wave. Reducing the air pressure in the pressings to
5 microns left the build-up to detonation unaffected. The position of
the shock Hugoniot for the pressings relative to the Hugoniot of the
solid crystal is discussed in terms of heat production during collapse
and possible reaction processes.

INTRODUCTION

A salient feature of initiation behavior in secondary high explo-
sives is the high sensitivity of a low-density granular pressing relative
to that of a homogeneous crystal of the same compound. Thus for
PETN approximately 110 kbar is required to detonate a large single
crystal,[1] whereas low-density pressings of small PETN crystals can
be initiated with shocks of a few kilobars.[2] For a shock wave to
change into a detonation wave, an energy-producing chemical reaction
must proceed fast enough to support the shock ahead of it. Many
workers have assumed that attaining a high reaction rate depends on
attaining high temperature; in fact, most of them have assumed the
Arrhenius law.[3] It has been shown[4] that the average temperature of

the material in a shocked granular explosive will barely suffice for high reaction rates in very insensitive materials, but for moderately sensitive secondary explosives it falls far short. Thus, the weak shock required to initiate granular PETN cannot raise more than a small fraction of the total mass of the pressing to the necessary temperature. Because of such instances, one is forced to postulate hot-spots, encompassing only a very small fraction of the mass in the pressing but containing the greater part of the energy.

Bowden has demonstrated that in impact processes hot-spots can be formed by (a) compression of interstitial gas, (b) intergranular friction, and (c) high-velocity flow.[5] Similarly, for shock initiation of granular explosives it has been proposed that hot-spots can be formed by compression of interstitial gases,[6] shock interaction within grains, intergranular friction,[7] jetting,[8,9] or stagnation.[10,11]

Cachia and Whitbread showed that removing the interstitial gas from tetryl left the gap-test sensitivity unchanged.[12] It has also been shown[2] that distance of shock travel before detonation is unaffected by the interstitial gas in granular PETN at density 1.0 g/cm^3. Although only a few granular explosives have thus far been investigated for interstitial gas effects, an effect of interstitial gas on initiation behavior is yet to be demonstrated. The situation with the other proposals is more equivocal and it may never be possible to eliminate any of them as possible mechanisms. Nevertheless, by studying a wide range of conditions it may be possible to establish definitely that some of them are active.

Failure diameter and variation of steady detonation velocity with charge diameter are controlled by chemical and hydrodynamic events in divergent flow behind the detonation front. Similarly, shock initiation characteristics are influenced by chemistry and flow patterns behind an initiating shock as well as by peak pressure. Presumably with adequate understanding of reactive flow, the relationships between various detonation properties could be written down and all could be derived from fundamental chemical and hydrodynamic properties of the material. Approximate theories have been developed for the effect of charge diameter on detonation velocity,[13-15] and thorough experimental studies have been completed in the case of homogeneous explosives.[16-18] A relationship has been developed between failure diameter, shock sensitivity, decomposition kinetics, and flow divergence.[19] The goal seems within reach.

A quite different situation holds for low-density granular explosives. The behavior of granular pressings under shocks of less than

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100 kbar peak pressure has not been investigated thoroughly, even for nonreactive systems. The hydrodynamics are much more complicated than for the homogeneous case. In a random arrangement of grains, intergranular friction, shock interaction, jetting, stagnation, and turbulence undoubtedly occur, and these details, probably not calculable, are likely to be the crucial events in starting chemical reaction. In such a complex physical situation several modes for chemical reaction may be possible.

As a contrast to PETN, on which some studies have been made, we have undertaken an investigation of the detonation and shock initiation of ammonium perchlorate, a low-energy explosive relatively insensitive even in the granular form at low densities. Extensive information on its thermal decomposition[20] recommends it among such explosives for an investigation in which sensitivity is to be related to chemical kinetics. Results on deflagration[21] of ammonium perchlorate may be useful in explaining growth from shock to detonation and determination of the minimum temperature for deflagration may have a bearing on shock sensitivity. So far our studies have been limited to pure ammonium perchlorate with a weight-median grain diameter of 13 μ at a loading density of 1.00 g/cm^3.

CALCULATION OF DETONATION CHARACTERISTICS

Chapman-Jouguet detonation properties were calculated for ammonium perchlorate over the loading density range from 0.55 to 1.95 g/cm^3 by means of the Ruby code developed by Levine and Sharples,[22] using the method of White, Johnson, and Dantzig in the equilibrium calculations.[23] The code solves simultaneously algebraic equations given by the shock conservation equations, the chemical equations, the Becker-Kistiakowsky-Wilson (BKW) equation of state, and the Chapman-Jouguet condition applying to detonations. The BKW equation of state has been used for detonation calculations for about twenty-five years,[24] empirically as a method for fitting well-known measurements and also for predicting properties of new explosives of a similar type. The calculation has been improved and adapted to computers by a number of workers.[25,26] Cowan and Fickett[27] obtained new values for the constants in the BKW equation by fitting their calculations to four explosives for which accurate values of detonation velocity and CJ pressure were available. The Ruby code uses the same constants.

The case of ammonium perchlorate is outside the range of conditions usually treated by Ruby code calculations. The energy of reaction is less than for most explosives, the calculations have been carried

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to lower densities than usual, the explosive contains chlorine on which there is little calculational experience involving accurately measured detonations, and carbon is absent so that the usually prominent energy-releasing components CO and CO_2 are missing from the products.

The assumed products were H_2O, H_2, N_2, O_2, NO, N_2O, NO_2, Cl_2, and HCl. The co-volumes of the first seven components were those used by Cowan and Fickett.[27] The co-volumes of the two chlorine-containing products were computed by the method customarily used for the other products. A <u>van der Waals</u> volume of the molecule was computed as a sphere with diameter equal to the largest molecule dimension. The co-volume was then obtained by multiplying this volume in A^3 by 10.46. The heat of formation of ammonium perchlorate was assumed to be -70.73 kcal/mole.[28]

Table I gives the calculated hydrodynamic variables. Table 2 lists the product compositions.

Table 1

C-J DETONATION CHARACTERISTICS FOR
NH_4ClO_4 CALCULATED BY RUBY CODE

ρ_0, AP (g/cm^3)	P_{CJ} (kbar)	T_{CJ} ($^\circ$K)	U_{CJ} (mm/μsec)
1.95	187	780	6.43
1.75	148	904	5.95
1.55	116	1039	5.49
1.35	88	1179	5.04
1.15	64	1322	4.59
0.95	45	1464	4.13
0.75	29	1600	3.67
0.55	17	1722	3.20

Table 2

DETONATION PRODUCT COMPOSITIONS FOR NH_4ClO_4 CALCULATED BY RUBY CODE

Moles Product Gas per gram NH_4ClO_4	Loading Density (g/cm³)							
	0.55	0.75	0.95	1.15	1.35	1.55	1.75	1.95
H_2O	1.69×10^{-2}	1.70×10^{-2}	1.70×10^{-2}	1.70×10^{-2}	1.70×10^{-2}	1.70×10^{-2}	1.71×10^{-2}	1.71×10^{-2}
H_2	2.80×10^{-9}	3.31×10^{-10}	2.35×10^{-11}	9.33×10^{-13}	1.77×10^{-14}	1.32×10^{-16}	3.00×10^{-19}	1.68×10^{-22}
N_2	8.58×10^{-3}	8.49×10^{-3}	8.46×10^{-3}	8.45×10^{-3}	8.42×10^{-3}	8.37×10^{-3}	8.29×10^{-3}	8.17×10^{-3}
O_2	4.23×10^{-3}	4.23×10^{-3}	4.23×10^{-3}	4.22×10^{-3}	4.20×10^{-3}	4.18×10^{-3}	4.14×10^{-3}	4.08×10^{-3}
NO_2	2.46×10^{-5}	3.63×10^{-5}	5.26×10^{-5}	7.55×10^{-5}	1.09×10^{-4}	1.58×10^{-4}	2.33×10^{-4}	3.53×10^{-4}
NO	4.23×10^{-5}	2.36×10^{-5}	1.11×10^{-5}	4.30×10^{-6}	1.30×10^{-6}	2.89×10^{-7}	4.30×10^{-8}	4.01×10^{-9}
N_2O	1.46×10^{-7}	1.54×10^{-7}	1.43×10^{-7}	1.18×10^{-7}	8.48×10^{-8}	5.19×10^{-8}	2.57×10^{-8}	1.01×10^{-8}
Cl_2	4.06×10^{-3}	4.23×10^{-3}	4.26×10^{-3}	4.26×10^{-3}	4.26×10^{-3}	4.26×10^{-3}	4.26×10^{-3}	4.26×10^{-3}
HCl	3.95×10^{-4}	6.51×10^{-5}	6.91×10^{-6}	4.20×10^{-7}	1.21×10^{-8}	1.27×10^{-10}	3.28×10^{-13}	1.36×10^{-16}

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EXPERIMENTAL

All of the experiments reported here used propellant grade ammonium perchlorate specified as MPD-28 A Type II. Analysis showed purity to be 99. 3% ammonium perchlorate or better in each sample. The material was reground to the particle size shown in Fig. 1.
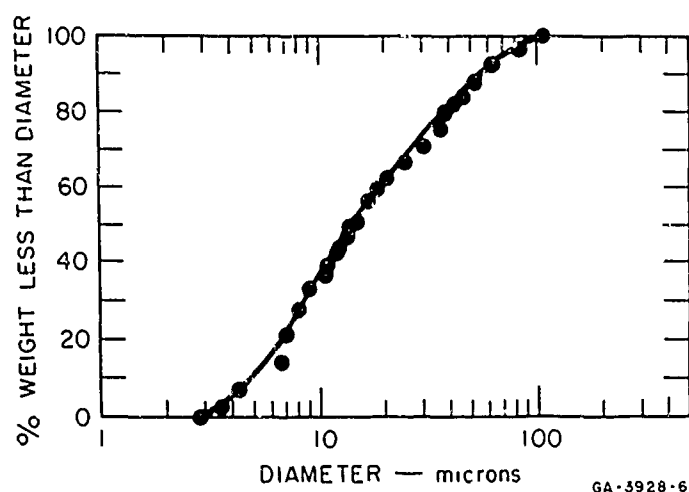

FIG. 1 PARTICLE SIZE DISTRIBUTION
OF AMMONIUM PERCHLORATE

The booster explosive was cast Composition B-3 (64/36:RDX/ TNT). Plane-wave generators made of cast Baratol [70/30:$Ba(NO_3)_2$/ TNT] and Comp B were obtained in two sizes known as P-40 (10 cm diam) and P-80 (20 cm diam).

Plexiglas used in the experiments was obtained cast from the monomers. The brass was obtained as the free machining type in the form of plates. Attenuators were machined to size, lapped, and polished.

A 35-mm rotating-mirror smear camera writing 3. 81 mm/µsec was used for all of the initiation experiments and some of the velocity measurements. Exposures were made on Eastman Tri-X film which was developed for $6\frac{1}{2}$ minutes in UFG developer. Other velocity measurements were made on raster oscilloscopes, either specially manufactured by Denver Research Institute to write at 2. 5 µsec per sweep or consisting of a separate Cordin Electronics 12. 5-µsec raster sweep component controlling a Tektronix 535 oscilloscope.

Determination of Detonation Velocity

Detonation velocity of ammonium perchlorate was determined at three charge diameters, 3.5, 10, 1, and 23.2 cm, with charge lengths ten times the diameter in each case. At 3.5 cm the charges were confined in cellulose acetate-butyrate tubing 1.5 mm thick in which elastic wave velocity was determined to be 1.9 mm/μsec, substantially below the detonation velocity of the ammonium perchlorate at this diameter. The charges were loaded in increments to 1.01 ± 0.01 g/cm^3 and boosted with a 4-inch gap-test donor consisting of a P-40 plane-wave lens and solid Plexiglas attenuator. Velocity in the charge was measured by ionization probes through the wall at 25.4-mm intervals. In this way "fires" from the gap test could be used to give velocity data after initiation phenomena had disappeared.

At the two larger diameters the ammonium perchlorate was loaded in cardboard rings one-half diameter high. These rings were stacked with a copper-foil ionization switch across the diameter of each segment, so that signals from the center of the charge could be recorded on the Cordin-Tektronix oscilloscope. The 10.3-cm charge was boosted with a 10-cm-diameter, 2.5-cm-thick Comp B slab initiated by a bursting-wire detonator and a 12.5 diameter by 6.3 mm RDX pellet. A velocity record was also obtained on the smear camera at this diameter through 1-cm holes punched at the center of each segment and faced on the inside with transparent tape. The 23.3-cm charge was boosted with a 20.3-cm by 5-cm Comp B charge initiated in the same way. Only oscilloscope timing was obtained on this shot.

At 3.5-cm-diameter thirteen shots yielded up to nine velocity determinations each. The shot-to-shot standard deviation was σ_s = 0.11. One experiment only was performed at each of the larger two diameters, 10.1 and 23.3 cm. The standard deviations of the incremental velocities σ_i were 0.07 and 0.05 mm/μsec, respectively. In Fig. 2 these results are plotted with the error indicated at $2\sigma_s$ for the 0.286 cm^{-1} reciprocal diameter data and $2\sigma_i$ for the two large shots. Extrapolation to infinite diameter gave 3.75 ± 0.15 mm/μsec, the uncertainty being estimated by extrapolation of the opposite extremes of the plotted errors.
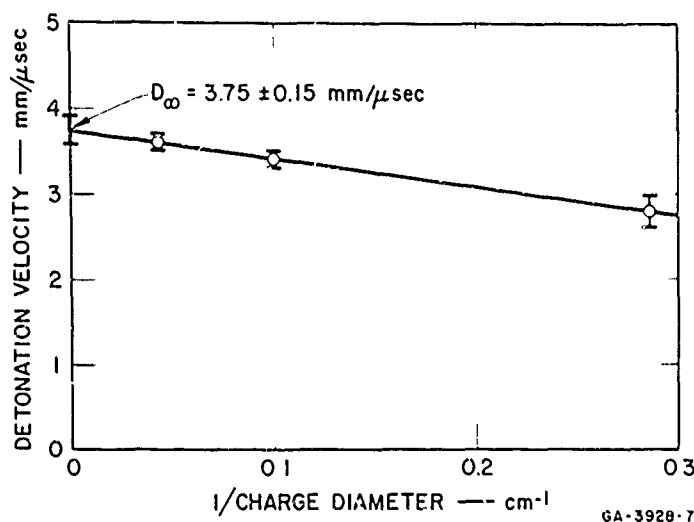
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FIG. 2 DETONATION VELOCITY OF
AMMONIUM PERCHLORATE
PLOTTED AGAINST RECIPROCAL
CHARGE DIAMETER

Minimum Shock for Initiation at 3.5-cm Diameter

The minimum pressure required to initiate steady detonation in long charges was qualitatively established by a variant of the gap method. The donor explosive was a P-40 plane-wave lens against which was placed an attenuator of solid Plexiglas. The ammonium perchlorate charge, 3.5 cm in diameter, packed as described in the section on velocity determination, was centered on the attenuator. The emergent wave at the attenuator-ammonium perchlorate interface was plane to 0.05 μsec over the test charge diameter. The Plexiglas free-surface velocity for the 50% gap thickness was determined by means of the moving image camera, using a parallel mirror above the surface. Light from an argon explosive flash was reflected into the camera until the reflectivity of the mirror was destroyed by arrival of the moving surface. The resulting camera record gave the time required for the surface to traverse the distance to the bottom surface of the mirror. From this a free-surface velocity of 1.00 ± 0.03 mm/μsec was obtained, corresponding to a calculated shock pressure in the Plexiglas of 16.5 ± 0.5 kbar. In the same experiment a Manganin resistance-wire pressure gauge[29] measured a confirming value of 17.0 ± 1 kbar for the Plexiglas shock pressure. The time profile of the wave at the interface was not determined.

The velocity of the wave generated in the ammonium perchlorate was first measured over the second 25.4-mm interval as 2.5 mm/μsec.

It became steady after about 75 mm at 2.81 ± 0.22 mm/μsec. Figure 3 gives pressure-particle velocity plots measured by two groups of experimenters for Plexiglas.[30, 31] We have assumed that the Plexiglas rarefaction curve is a mirror reflection of the Hugoniot. A $\rho_0 U_s$ line corresponding to the 2.5 mm/μsec measured in the second interval intersects the rarefaction curve at 14 kbar in the ammonium perchlorate. Thus 14 kbar is the minimum pressure which will initiate this material at this diameter with the pressure-time profile delivered by this booster-attenuator system. Data to be presented in the next section show that initiating shocks in this particle-size ammonium perchlorate at this density accelerate very little until just before rapid build-up to full detonation velocity.
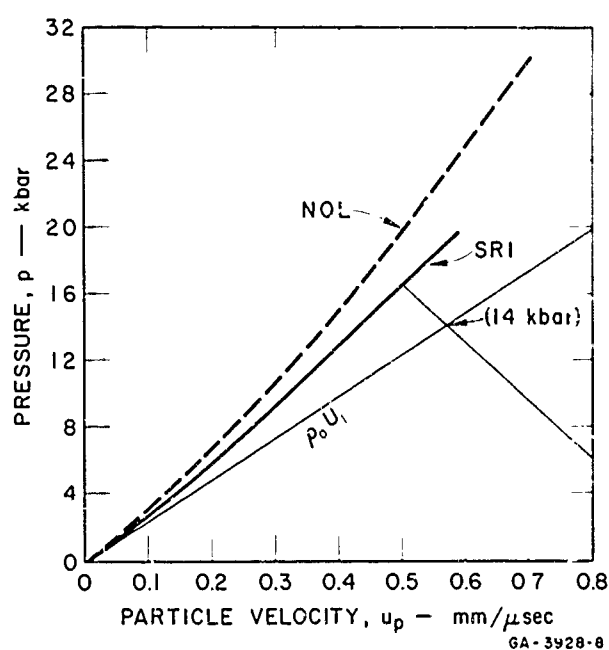

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FIG. 3   HUGONIOTS FOR PLEXIGLAS
NOL curve is from Ref. 30, SRI
curve is from Ref. 31. The $\rho_0 U_i$ line
is for ammonium perchlorate at
density 1.0 g/cm³ and intersects
the Plexiglas expansion curve
at 14 kbar

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Plane-Wave Initiation Measurements

Shock initiation of ammonium perchlorate was studied for approximately flat-topped shocks at about 24 kbar. For this pressure, transition to steady detonation occurs in times which are long enough to establish the incoming wave velocity but short enough that the transition occurs before the initial shock is influenced by reflections or rarefactions.

The driver system for the majority of the shots was a P-80 plane-wave lens detonated directly against a 1/2-inch-thick brass driver plate. The duration of the initial pulse before reflections accelerate the brass was determined by observing with a moving-image camera a reflected image of a wire on the polished driver plate.[32] For this driver system the free-surface velocity was constant for 12.5 μsec before the first reflection arrived, as is shown in Fig. 4. The long reverberation time was not the result of spalling, as the brass was recovered in one solid piece.
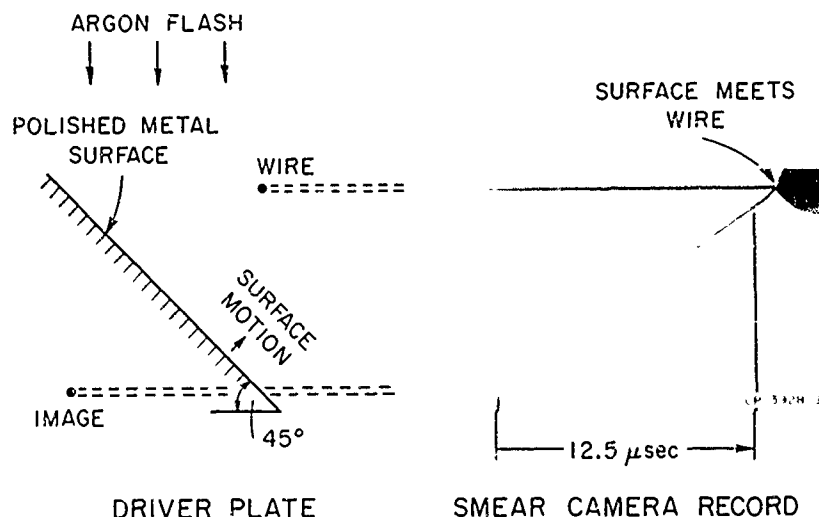
FIG. 4 MEASUREMENT OF BRASS DRIVER PLATE FREE SURFACE MOTION BY THE WIRE REFLECTION TECHNIQUE. Experimental arrangement is shown at left and the resulting film at right.

Pellets of ammonium perchlorate were formed at loading density 1.00 ± 0.005 g/cm^3 by packing the powder into Plexiglas rings, whose diameters were at least three times their height. Pellets of various heights were arranged on the brass driver plate in two rows so they could be photographed through two parallel slits by a moving-image camera. The wave was sufficiently plane over an area approximately 15 cm in diameter that as many as four pellets could be observed on

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one slit, depending on their diameter and the other measurements to be made.

For most of the experiments one-half of the surface of each pellet was covered with a thin sheet of Plexiglas. On small pellets a 1.6 mm thickness was adequately rigid, but for large pellets 3.2 mm was necessary. Over the covered half of the pellets an angled mirror was placed for measurement of the free-surface velocity of the Plexiglas. An explosive argon flash was reflected specularly from the mirror into the camera and also served to illuminate the uncovered surface of the pellet.

The overall array of pellets of various lengths is shown in Fig. 5. The following were directly indicated by the films: (a) arrival time of the shock at the bottom of the pellets, (b) planarity of the wave, (c) free-surface velocity of the driver, (d) arrival times at the tops of the pellets, (e) wave shapes at the tops of the pellets, and (f) free-surface velocity of the Plexiglas sheet. A typical record showing these features is shown in Fig. 6, and for clarity a line tracing of this record is given in Fig. 7.
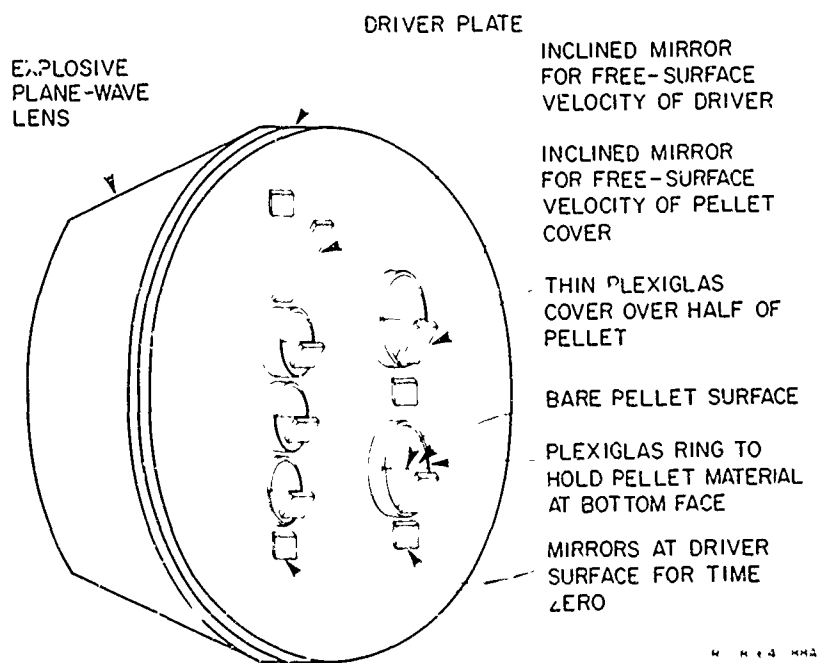

FIG. 5 CHARGE ARRANGEMENT FOR A TYPICAL SHOT TO INVESTIGATE INITIATION CHARACTERISTICS OF AMMONIUM PERCHLORATE. Two rows of pellets are photographed simultaneously through double camera slit.
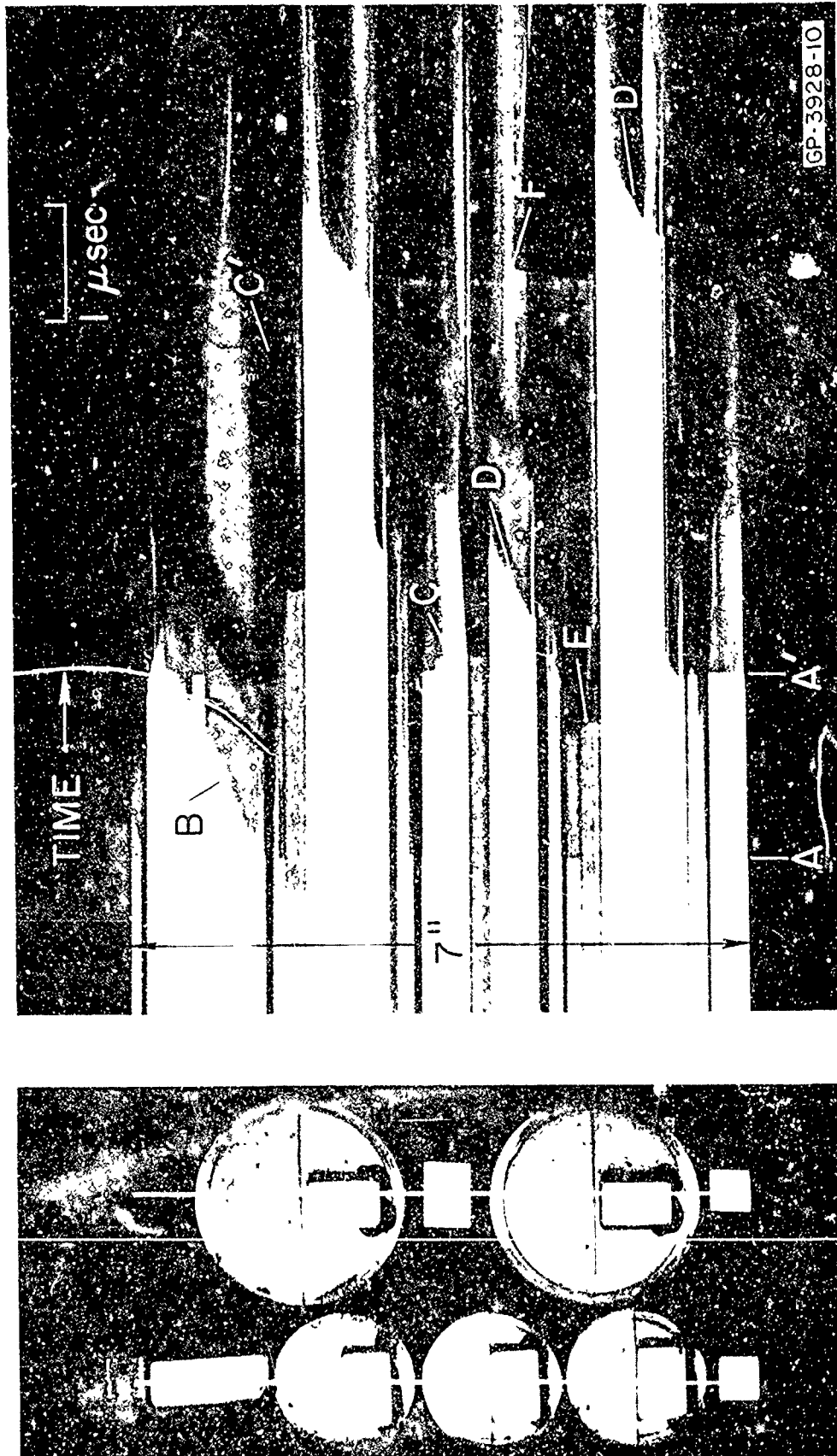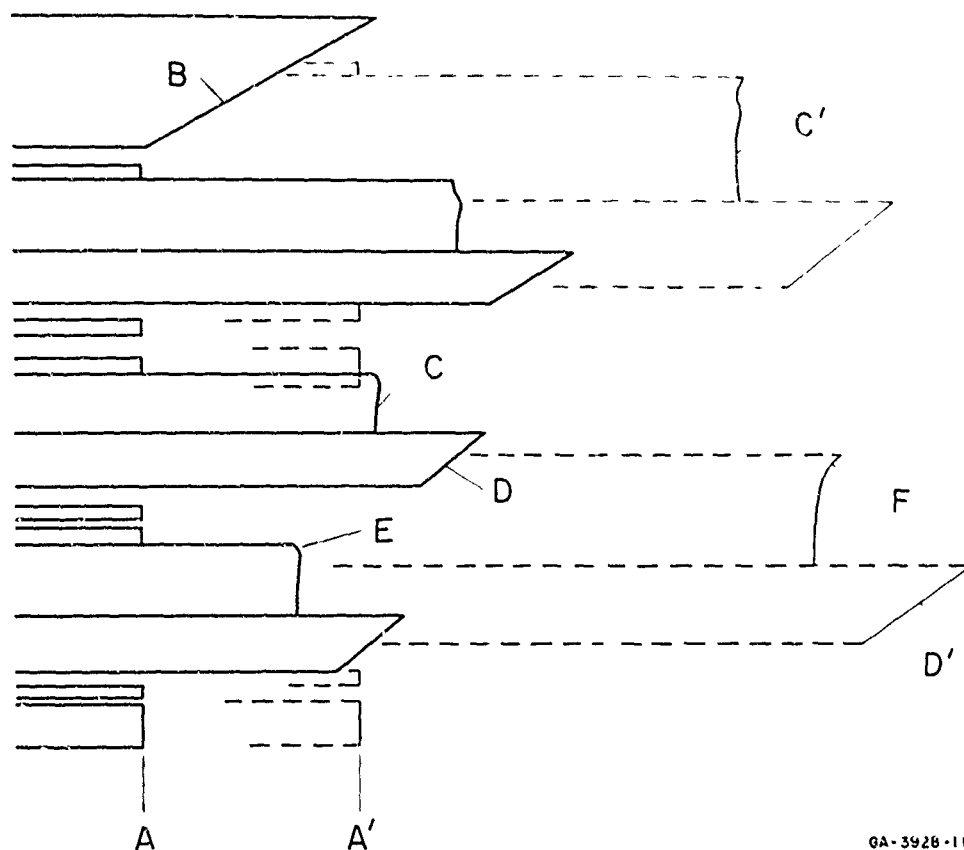
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FIG. 6 SMEAR CAMERA RECORD OF PELLET ARRANGEMENT DIAGRAMMED IN FIG. 5
At left is the still picture, at right the time record

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FIG. 7 DRAWING OF SMEAR CAMERA RECORD CORRESPONDING
TO FILM IN FIG. 6

Signals caused by the arrival of the shock at the surface of the
driver plate are indicated by the lines marked A and A' for the two
slits, respectively. From these signals an indication of planarity is
obtained. When there is some variation in the arrival time of the wave,
individual signals at the bottoms of the Plexiglas rings can be used for
their respective pellets. The free-surface velocity of the driver is
obtained from the angle of the trace marked B.

A drop in intensity of scattered light from the uncovered half of
the pellet indicates the arrival of the shock at the top surface. Two
such signals, one on each slit, are marked C and C'. On the covered
half of the pellets the free-surface velocity of the Plexiglas is obtained
from the angles of traces such as D and D'.

From these primary data the following derived quantities may be
calculated: (a) driver plate pressure, (b) wave pressure at the bottom
of the pellet, (c) shocked density at the bottom of the pellet, (d) wave
transit time, (e) wave pressure at the top of the pellet, (f) shocked
density at the top of the pellet.

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Figure 8 gives a plot of wave transit time versus pellet thickness. The error lines show two standard deviations with three to five measurements having been made at each point. The incoming wave has a velocity of 2.75 mm/μsec. After about 15 mm of travel the wave velocity increases. Establishing the precise time at which detonation is achieved is practically impossible. However, at whatever point the transition occurs the velocity will thereafter be 3.75 ± 0.15 mm/μsec, the value determined above as D_{∞}, as long as the wave remains plane. A line of this slope has therefore been fitted to the points for pellet thicknesses above 15.5 mm. A thickness-time plot for an overdriven wave has also been given in Fig. 8.
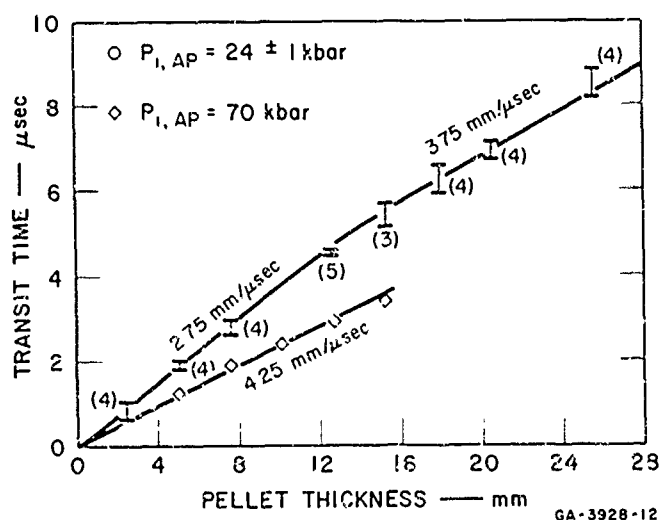
FIG. 8   TIME-DISTANCE PLOTS OF DATA OBTAINED FROM AMMONIUM PERCHLORATE PELLETS WITH ENTERING SHOCKS AT 24 kbar AND 70 kbar

The wave shapes marked E and F in Figs. 6 and 7 indicate the effects of the Plexiglas retaining rings. For a short pellet 5 mm in height (at E), the wave next to the Plexiglas leads the central part of the wave because the wave velocity in the center is less than in Plexiglas. For a long pellet 15 mm in height (at F), the wave next to the Plexiglas lags behind because the wave velocity in the ammonium perchlorate is greater than in the Plexiglas. The shock velocity in Plexiglas should be 3.6 mm/μsec near the driver plate but would fall in the long retaining rings to sound velocity, while the velocity in the ammonium perchlorate increases from 2.75 to 3.75 mm/μsec.

The pressure at the top of the pellet p_i is calculated from the pressure transmitted to the Plexiglas by use of the expression[33, 34]

$$P_i = P_t \frac{\rho_{oPl} U_t + \rho_{oAP} U_i}{2\rho_{oPl} U_t}$$

where

ρ_{oPl} is the density of the unshocked Plexiglas,

ρ_{oAP} is the density of the unshocked ammonium per-
chlorate pressing,

U_i is the velocity of the shock in the ammonium
perchlorate at a given pellet height,

U_t is the velocity of the shock transmitted to the
Plexiglas, and

P_t is the pressure in the Plexiglas calculated
from the free-surface velocity of the Plexiglas.

This technique of studying a developing detonation by observing wave pressure is a variant of that first used by Fauquinon[35] who measured the shock velocity induced in Plexiglas blocks by receptor charges of various lengths and from that estimated the wave pressures.

Figure 9 gives the wave pressure at the top of the pellet as a function of pellet thickness. The value at zero thickness is the enter-ing pressure calculated from the brass free-surface measurement. In the ammonium perchlorate the wave pressure increases over the first 15 mm and then reaches a value of about 55 ± 10 kbar. The shape of this plot depends on the slope of the curve in Fig. 8, and thus is not an independent experimental confirmation that build-up is taking place. A simpler indication is given by the trend in Plexiglas particle veloci-ties. The average of eleven measurements made on the four shortest pellets was 1.01 mm/μsec with a standard deviation $\sigma_i = 0.09$. The average of eleven measurements made on pellets 17.8 and 20.4 mm long was 1.23 mm/μsec with $\sigma_i = 0.26$.

An auxiliary experiment was carried out to confirm that the 24-kbar plane-wave initiation system would lead in a long charge to a wave that could be identified as a detonation by its steadiness and light output. An ammonium perchlorate rate stick 10.16 cm in diameter was packed in the cardboard rings described for the velocity determin-ations, but now provided with a narrow vertical cellulose acetate window
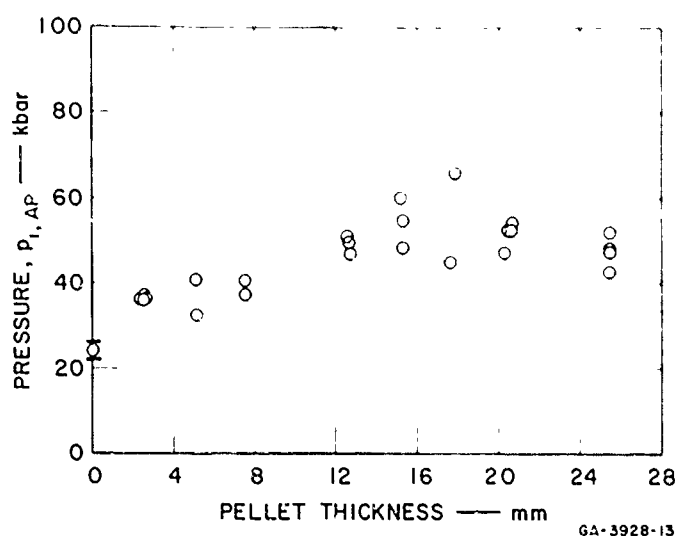
FIG. 9 PRESSURES CALCULATED FROM FREE
SURFACE VELOCITIES OF PLEXIGLAS
AT TOP OF AMMONIUM PERCHLORATE
PELLETS

of the same thickness as the tube wall to permit observation with a moving-image camera. Increments were stacked to a height of 30.5 cm. Initiation was by a P-80 plane-wave lens and a 1/2-inch-thick brass driver plate. The initiating system thus provided the 24-kbar input wave used in the plane-wave ''et initiation experiments.

At the start of the trace near the driver plate a low-velocity region was observed, but after about 15 mm of travel the trace became straight at 3.26 mm/μsec, the steady velocity for a 10-cm-diameter ammonium perchlorate charge at 1.0 g/cm^3.

At the top of the charge, free-surface velocity of a 3.2-mm-thick Plexiglas cover plate was measured with the inclined mirror method. The wave was curved so that the free-surface velocity could be measured only at the axis and even there with no great accuracy. The calculated wave pressure was 59 ± 10 kbar.

Vacuum Experiments

A chamber with a glass face plate was built over the brass driver plate of four of the pellet shots so that the initiation behavior of ammonium perchlorate could be studied when most of the interstitial air had been removed. In order to permit a valid comparison without a large number of shots, similar shots were prepared from what were believed to be identical components. Construction of a vacuum shot and its control were carried forward simultaneously and the two shots were fired in succession with as little delay as possible.

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The data are listed in Table 3. The differences in transit time
between the vacuum shots and the corresponding one-atmosphere shots
are small relative to the error limits shown in Fig. 8 and apparently
of random sign.

Table 3

COMPARISON OF x, t DATA FROM SHOTS
UNDER VACUUM AND AT ONE ATMOSPHERE

Pressure / x mm	t μsec		
	1 atm	6 μHg	5 μHg
	Shot 10,608	Shot 10,607	
2.49		0.98	
2.53	0.96		
5.10		2.01	
5.15	2.01		
7.62		2.85	
7.62	2.82		
12.62		4.50	
12.68	4.57		
15.24	5.50		
15.25		5.49	
17.75		6.09	
17.75	6.16		
	Shot 10,899		Shot 10,960
20.40			7.02
20.45	6.98		
25.40			8.60
25.50	8.73		

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DISCUSSION

The value 3.75 ± 0.15 mm/μsec for the ideal detonation velocity compares well with 3.70 mm/μsec found by Anderson and Pesante[36] for 12-μ ammonium perchlorate by extrapolation of data in the diameter range between 1.9 and 10.2 cm. For a low-energy insensitive explosive it is possible that velocity data collected at what might normally be considered large diameters will be in a nonlinear part of the reciprocal diameter plot. For this reason we have fired one shot at over 23 cm diameter even though it had to be fired underground. The data from this shot confirm the line established at the smaller diameters and, therefore, we believe the extrapolation is valid and that D_{∞} represents a true experimental estimate of the ideal detonation velocity.

The velocity computed by the Ruby Code (4.25 mm/μsec, Table 1) is significantly higher than the experimental determination. The calculation has been established by comparing calculated and experimental values of detonation velocity and pressure and adjusting equation-of-state constants until optimum agreement is produced. Checks have been possible on a number of CHON explosives[26] so that adequacy of the equations and the parameters is well-established for this class. Any explosives at density below 1.2 g/cm^3 are not accurately calculated with this equation of state with the present constants. Calculations involving chlorine may involve further modifications. Therefore, the agreement between experimental and calculated values of velocity is believed to be as good as expected. Any noticeable improvement would involve a considerable series of accurate measurements on ammonium perchlorate and similar compounds and perhaps shock measurements on liquid HCl and Cl_2.

Minimum Pressure for Initiation at 3.5 cm Diameter

The gap-test results were obtained with a 10-cm-diameter Plexiglas attenuator and a 10-cm plane-wave lens. The wave shape as it left the Plexiglas was plane over the 3.5-cm-diameter area occupied by the test charge. The wave-speed traces of the disturbance in the ammonium perchlorate obtained at edge of the charges became straight after about 70 mm and this indicates that initiation phenomena lasted almost this long. Since the wave shape of the shock was changing and the pressure falling, it seems reasonable that 70 mm is close to the longest initiation zone that could be observed at this diameter.

Our value of 14 kbar may seem to be in conflict with a value of 6 kbar reported by Jaffe and Price.[27] However, it is believed this conflict is only apparent since the Jaffe and Price experiments differed

from ours in several important respects: (a) lower density, $0.85 \, g/cm^3$, (b) larger particle size, (c) a charge container of steel in which sound velocity is higher than the detonation velocity of ammonium perchlorate.

Plane-Wave Initiation

Ammonium perchlorate was chosen for study because it is insensitive and low-powered. The insensitivity leads directly to a relatively high velocity for the initiating shock, the low power leads directly to a low detonation velocity, and the combination of these two factors leads to a very real experimental difficulty in determining when initiation occurs. It has been impossible to establish the final detonation velocity from measurements in the pellet experiments alone because a certain amount of error in the x, t data is inevitable, and because the longest pellets may have been perturbed by edge effects. Therefore, a line with slope equal to the ideal velocity D_{∞} was adjusted (visually) in intercept to fit the data above 15 mm. There is some slight evidence in the x, t plot that the transit times on the pellets of greatest length have been increased by edge effects.

Pressure Measurements

Additional evidence of initiation was obtained by the pressure measurements. It is impossible in practice to make free-surface measurements on the explosive itself when it is at low density in the granular form. Instead, the microscopically complex wave in the pressing induced a shock in Plexiglas. On this material, free-surface measurements can be made easily and converted to the pressure in the ammonium perchlorate by solving the Plexiglas-explosive interface equation. Accurate measurements of this kind would require very painstaking work and a careful study of the effect of Plexiglas thickness. We have actually accomplished only rather gross measurements in which it was assumed that effects of wave shape might lower the pressure only about 10 or 20%. The results in Fig. 9 support our interpretation of the x, t data. Note that there is an indication that the pressure is falling off in the same interval. A further indication was the wave shape observed for the longest pellets, which in most cases had only a very small plane region at the center and in some had none at all.

Effect of Vacuum on Initiation

The vacuum experiments give evidence as to whether the gas compression mechanism can be responsible for shock initiation of ammonium perchlorate. The data in Table 3 show that within the accuracy of our experiments the build-up of the wave is unaffected by

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the presence or absence of interstitial gas. The exact interpretation that can be placed on this statement needs some discussion.

We evacuated the pellets rather than filled them with a high specific-heat gas because the results are more definitive. When the mass of gas is reduced by a factor of 10^5 as in these vacuum experiments, the total energy for transfer to the grains is reduced by a roughly similar amount. Thus, if calculations of grain surface temperatures are in question, changes in the heat transfer coefficient are avoided. If the equilibrium temperature of small grains is being calculated, reduction of the energy available has a direct effect.

The overall shock initiation process in granular explosives should probably be considered to consist of at least two phases: (1) the primary initiation process--creation of small nuclei of decomposition, and (2) the growth process--acceleration of the shock to the point where it becomes a steady detonation. The fact that we cannot tell the difference between normal atmospheric air density and 10^{-5} of this density in the arrival times of the shock at various positions during growth of the wave indicates at least that the interstitial gas does not affect the build-up process. This is no cause for surprise, since even for a grain-burning mechanism the rate during the shock-growth period need not depend on the ambient pressure that existed before the first hot-spots were created. It is, nevertheless, a fact that the interstitial gas does not affect the rate of build-up of a 24-kbar shock in ammonium perchlorate at 1 g/cm^3.

Our vacuum experiments also imply something about the primary initiation process. The very least that can be said is that this primary process does not depend uniquely on the presence of interstitial gas -- an explosion did occur. Most theoretical calculations of the heat transfer to the solid from the gas will be very seriously altered by changing the density and total mass of the gas by a factor of 10^5. It might be maintained that the gas compression mechanism was active at one atmosphere but another mechanism took over at 5 μ Hg. However, it is very unlikely that substitution of mechanisms would occur so precisely. The real problem is to show why the process active at 5 μ Hg, which clearly exists but does not involve the interstitial gas, is not adequate to explain initiation at one atmosphere.

Since our result was obtained at 24 kbar, considerably above the minimum pressure necessary for initiation, it might also be maintained that initiation by lower pressure shocks, 14 kbar for instance, may be controlled by the interstitial gas.

Hugoniot of Ammonium Perchlorate Pressings

In Fig. 10 are four circles representing a p, v point from the plane-wave initiation experiments at 24 kbar, a point from the gap-test experiments at 14 kbar, and two higher pressure points which almost certainly correspond to complete reaction of the ammonium perchlorate.

Zel'dovich and Kompaneets are reported[38] to have developed the theory for Hugoniot curves of porous materials using the Mie-Grüneisen equation of state. They assumed that (1) the pressing required zero compaction force, (2) the specific internal energy of the crystal equaled that of the granular material, (3) the pressing could be treated as a homogeneous fluid, ignoring granularity. The general form of the Hugoniot for a pressing of fairly high porosity is shown by the dashed line in Fig. 10. The exact shape and position of the curve depends on the equation of state of the solid material and the porosity of the pressing.

Russian experimentalists have found that the dashed curve is not realized, but that the top part of the curve bends toward normal crystal density as illustrated by the dotted curve. In the case of powdered metals, this occurs at relatively high pressures and is ascribed to electron effects and change in the lattice specific heat. Recently data have been reported[39] on granular pressings of ionic crystals which are cases closer to that of ammonium perchlorate. However, in all this Russian work the main interest has been extremely high pressures.

In our present data on ammonium perchlorate the experimental point at 14 kbar lies at a larger volume than that of the solid crystal, and from this we conclude that the Hugoniot is positively sloped as predicted by Zel'dovich. However, since the volume at 24 kbar is smaller than at 14 kbar, we must conclude we are in a region where pressure is double-valued. It thus becomes of some importance to determine if, in fact, the Hugoniot assumes a positive slope below 10 kbar and if the volume approaches that of the crystal under the action of very weak shocks.

Also in Fig. 10 is a square which represents the volume expected from static pressure at 2 kbar. Such a pressure is not negligible relative to weak shocks.

We have attempted two shots at very low pressure. These experiments have turned out to be more difficult than originally anticipated because of a short reverberation time in the multilayered attenuator, a poorly defined brass Hugoniot at very low pressures, poor
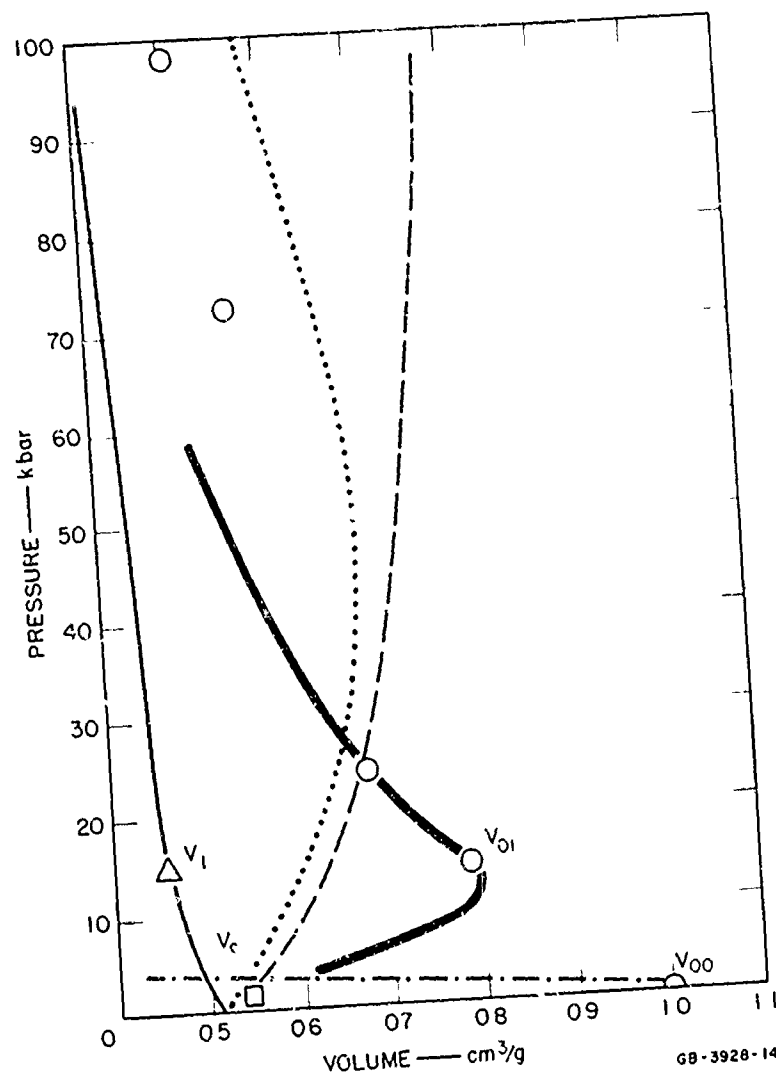
FIG. 10 HUGONIOT CURVES FOR AMMONIUM PERCHLORATE

○   Measurements on NH_4ClO_4 pressings at four shock pressures.

□   Static compression of granular pressing.

————   Assumed Hugoniot of ammonium perchlorate crystal.

— — ·—   Typical Hugoniot of porous pressing predicted by Zel'dovich.

· · · · · · ·   Typical Hugoniot of pressing found by Russian experimenters.

— · — · —   Rayleigh line for low-pressure shock in ammonium perchlorate pressing.

━━━━━   Hugoniot proposed for ammonium perchlorate pressing.

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quality optical signals from the emergence of very low intensity shocks, and difficulty in producing thin pellets of good quality. Nevertheless, it is clear that the shock velocity over the first 3 mm of travel in the pressing is in the neighborhood of 0.75 mm/μsec, only slightly above sound velocity, 0.54 mm/μsec.[40] The Rayleigh line corresponding to this velocity is drawn at the bottom of the graph in Fig. 10. A pressure between 2 and 3 kbar was obtained from the free surface velocity of the brass by the graphical solution of the brass-perchlorate interface equation.

Taking into account the four data points that we have, the fact that 2 kbar will compress the material to 95% crystal density, and the indications of the preliminary low-pressure shock experiments, we have drawn the Hugoniot of the pressings (the heavy solid line) to resemble those used by the Russian experimenters. The main difference between this curve and the Russian Hugoniots is the low pressure at which the high-volume bulge occurs. This, at about 10 kbar, is so low that it must have an explanation in addition to the one offered for the higher pressure bulge in inert materials. In general terms, however, the explanation is the same. The material exists at the two volumes V_1 on the crystal Hugoniot and V_{01} on the Hugoniot for the pressing not only because the specific internal energy is higher at V_{01} than at V_1, but also because the percentage of internal energy in the thermal term is higher at V_{01}.

The pressing is considered in the theory to be homogeneous, that is, the material is a fluid at the expanded state V_{00}. The positive slope of the Hugoniot arises from irreversible work during compaction. The heterogeneity itself can be expected to cause heating through jetting, turbulence, and stagnation. In this sense the shape of the Hugoniot of the pressing is an indication of the number and temperature of hot-spots.

The upper part of the Hugoniot of the pressing has been drawn below the points at 70 and 98 kbar because these almost certainly lie on the fully reacted Hugoniot. However, it is not clear that the points at 24 and 14 kbar represent inert material--some reaction may occur very rapidly in the hot-spots. In fact, release of chemical energy is an excellent candidate among possible explanations of the large final volumes on the porous Hugoniot. Detailed comparison of the ammonium perchlorate curve with that of an inert that is mechanically similar may indicate the degree of chemical reaction.

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